RE-VISITING THE ELECTRONIC ENERGY MAP OF THE COPPER DIMER BY DOUBLE-RESONANT FOUR-WAVE MIXING

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The copper dimer is one of the most studied transition metal (TM) diatomics due to its alkali-metal like electronic shell structure, strongly bound ground state and chemical reactivity. The high electronic promotion energy in the copper atom yields numerous low-lying electronic states compared to TM dimers with *(*d)-hole electronic configurations. Thus, through extensive study the excited electronic structure of Cu_2 is relatively well known, however in practice few excited states have been investigated with rotational resolution or even assigned term symbols or dissociation limits.

The spectroscopic methods that have been used to investigate the copper dimer until now have not possessed sufficient *spectral* selectivity, which has complicated the analysis of the often overlapping transitions. Resonant four-wave mixing is a non-linear absorption based spectroscopic method. In favorable cases, the two-color version (TC-RFWM) enables purely optical mass selective spectral measurements in a mixed molecular beam. Additionally, by labelling individual rotational levels in the common intermediate state the spectra are dramatically simplified.

In this work, we report on the rotationally resolved characterization of low-lying electronic states of dicopper. Several term symbols have been assigned unambiguously. De-perturbation studies performed shed light on the complex electronic structure of the molecule. Furthermore, a new low-lying electronic state of Cu_2 is discovered and has important implications for the high-level theoretical structure calculations performed in parallel. In fact, the *ab initio* methods applied yield relative energies among the electronic levels that are almost quantitative and allow assignment of the newly observed state that is governed by spin-orbit interacting levels.